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(54) Paper-coating compositions containing dyed filler

(57) Coloured, coated paper is obtained by applying to paper an aqueous coating composition containing a filler, which has been dyed with a water-soluble polycationic dyestuff, and a binding agent. The coated paper is particularly useful as xerographic copying paper.

GB 2 117 783 A

SPECIFICATION

Improvements in or relating to organic compounds

In the preparation of paper it is common practice to use fillers which are generally white inorganic pigments. Such papers are frequently dyed, for example with direct, acid or basic dyestuffs. Direct dyes are used predominantly for dying of paper which is wood-free or has a low good content, whereas basic dyes are suitable for dyeing paper of high wood content. It is desirable for the dye to bind as strongly as possible to the paper fibres, to avoid subsequent bleeding of the colour.

Fillers may be added to the pulp from which the paper is made, but high quality papers are often coated with a composition comprising an aqueous paste of filler together with a binding agent, for example starch or a synthetic resin, and optionally a dispersing agent. For coated paper, a further method of colouring the paper is to apply to it a coloured coating composition, generally containing one or more coloured pigments either as sole filler or together with a white pigment. However when a mixture of white and coloured pigments is used, these pigments frequently migrate to different extents during the drying process, which can lead to non-level dyeings. Furthermore, the use of pigments is less efficient than that of soluble dyes, particularly for deep shades.

It is known to add water-soluble dyestuffs to coating compositions containing a white pigment. This gives a number of disadvantages, however, particularly for high quality paper. This is particularly due to insufficient exhaust of the dye on to the substrate, leading to unsatisfactory fastness properties. Quite generally, for any water-soluble dyes used together with white pigments, the differences in migration properties, particularly when a mixture of dyes is used, lead to non-level dyeings and variations in depth. In addition, particularly with basic dyes, light fastness is poor; and the addition of cationic dyes to an anionically stabilized coating system often causes precipitation.

It has now been found that disadvantages can be overcome by dyeing the filler with a water-soluble polycationic dye before incorporating it into coating composition. Particularly good results can be obtained by the use of selected groups of cationic dyestuffs, as described below.

Accordingly, the present invention provides a coloured coating composition for paper comprising an aqueous paste or dispersion of a filler which has been dyed with a water-soluble polycationic dyestuff, together with a binding agent.

Suitable fillers may be organic, for example urea/formaldehyde condensation products such as the commercially available products Pergopak® (Ciba-Geigy) or Lytron® (Monsanto), but are preferably inorganic. Preferably the filler is a white inorganic pigment. Examples are finely divided silicates, e.g. kaolin (china clay), talc (soapstone), diatomite (kieselguhr or filter earth) french chalk, asbestine, calcium silicate (obtainable in particularly suitable form by mixing cold concentrated $CaCl_2$ solution with cold concentrated sodium silicate solution), quarz sand and asbestos; sulphates e.g. gypsum, annaline, lenzine, satin white (calcium sulphoaluminate), heavy spar and permanent white (both $BaSO_4$); carbonates e.g. calcium carbonate (e.g. chalk), magnesite, whiterite, white lead, dolomite and calamine; oxides or hydroxides e.g. alumina, bayrites, titanium dioxide, slaked lime, burned magnesia and zinc white; sulphides e.g. lithopone and zinc sulphide; and sulphites e.g. calcium sulphite. Preferred fillers for dyeing with cationic dyes are kaolin, calcium carbonate, talc, permanent white and titanium dioxide, especially kaolin, calcium carbonate and talc. It is surprizing that even cheap fillers such as chalk give excellent results, particularly with the selected groups of cationic dyes.

By polycationic dyestuffs is meant dyestuffs having at least 1.3 cationic groups (quaternary or protonated nitrogen atoms) per dye molecule, whereby a non-integral number of cationic groups is to be understood as an average value for the molecules of the dyesuff in question. The dyestuffs may also contain anionic groups, particularly sulphonic acid groups, but if any such are present, then the number of cationic groups per molecule must be at least one greater than the number of anionic groups per molecule. Expressed numerically, if there are x cationic and y anionic groups per molecule, then $x \geq 1.3$ and $0 \leq y \leq (x-1)$. More preferably the dyestuffs are biscationic.

The dyes may be metallized or metal free, but metal complex dyes are preferred, more preferred being 1:1 and 1:2 metal complex azo dyes. For 1:2 complexes, containing two dyestuff units per metal atom, the requirement of at least 1.3 cationic groups per molecule applies to each dyestuff unit and not to each molecule of complex. As well as azo dyes, other cationic dyes, for example phthalocyanine (preferably copper phthalocyanine) dyes and anthraquinone dyes may be used. Dyes containing a fibre-reactive group may also be employed.

Preferably the dyes have, as the metal-free cation, a molecular weight of at least 400, more preferably 500-1000. Preferably they are substantive to the filler to be used, that is, they exhaust from an aqueous solution containing 1% dyestuff, based on the weight of filler, on to the filler, at 20-90°C and without the use of dyeing assistants, to an extent of at least 90%. More preferred dyes are those which give a high degree of exhaust on cotton, as measured by the following test: the dye should give an exhaust ratio (ratio of dye exhausted on to substrate to total dye in bath) of 90-100% as defined by DIN 54000 or ISO RIOS/I 1959, part 1, when dyed on to mercerised cotton at 1/1 standard depth from a boiling aqueous electrolyte-free bath at 20:1 liquor to goods ratio, dyeing time 90 minutes.

Dyestuffs meeting these conditions are predominantly those having peripheral or terminal cationic groups

in the molecule. One preferred group of dyestuffs are phthalocyanine dyestuffs containing two or more cationic groups which are attached to the periphery of the planar phthalocyanine ring system. A further preferred group of dyestuffs have a substantially linear structure comprising three or more homo- or hetero-aromatic rings or fused ring systems joined directly or by bridging groups in such a way that there are two terminal rings or ring systems and one or more medial rings or ring systems, there being on average at least 1.3 cationic groups per molecule attached to terminal rings or ring systems, and none elsewhere. In a more preferred group there are two or more, preferably two cationic groups per molecule, one or more, preferably one on each terminal ring or ring system and none elsewhere.

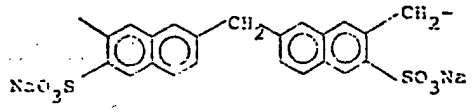
Dyestuffs having the above properties and structural features are known in the art, and are disclosed for example in the following published patents and patent applications: German published applications 1 061 010, 1 064 661, 1 621 702, 2 250 676, 2 251 041, 2 604 699, 2 627 680 and 2 810 246; US Patents 3 709 903, 3 784 599, 3 839 426, 3 933 787, 3 935 182, 3 996 282, 4 046 502, 4 103 092, 4 146 558, 4 153 598 and 4 213 897; and European published applications 13 751, 14 677, 14 678, 15 232, 15 233, 15 511, 16 726, 24 321, 24 322, 34 725, 38 299, 54 616, 56 574, 62 824, 62 825, 63 261 and 65 595. Particularly preferred cationic dyestuffs are those disclosed in published British Patent Applications 2 076 421A, 2 081 734A, 2 082 615A and 2 104 538A, British Patent 2 019 873 and published European Application 41 040, the contents of which are incorporated herein by reference.

The dyed filler may be prepared by making the white pigment into a paste with water, or by dispersing it in water with the aid of a nonionic and/or cationic dispersing agent, the solids content of the resulting paste or dispersion being from 0.1% to 90% by weight, preferably 10-70%. To the stirred paste or dispersion is then added a 0.1-70% wt. aqueous solution, preferably a 5-40% solution, of the cationic dyestuff, at a temperature of 1-100°C, preferably 20-70°C. The required dyeing time is from 10 seconds to 60 minutes, a time of 1-20 minutes generally being sufficient. Optionally a conventional fixing agent may be used.

Alternatively, the dry white pigment may be mixed thoroughly with dry dyestuff in powder or granulate form, and the resulting mixture made into a paste with water or dispersed in water with the aid of a dispersing agent. The dyeing conditions are then the same as given above.

The resulting dyed pigment may be isolated e.g. by filtration, centrifuging or spray drying, and the product further washed and dried if required. Alternatively the dyed slurry may be used directly in the next step.

In the preparation of the coating composition, it is desirable to add 0.1-10% of a dispersing agent e.g. a polyphosphate or polyacrylate. Other suitable dispersing agents include condensation products of sulphonated aromatic compounds with aldehydes, e.g. condensation products of sulphonated naphthalene, diphenyl, diphenyl oxide and related products with formaldehyde. The preferred dispersing agents are condensation products of β-naphthalene sulphonic acid with formaldehyde, containing units of structure



These dispersing agents, which are known, may also be used in combination with other dispersing agents such as polyacrylates, particularly when large amounts of dyestuff are used, or low coating viscosities must be attained.

The coating composition may contain any conventional aqueous binding agent dispersion or emulsion, for example those based on starch, acrylates, butadiene/acrylonitrile, butadiene/styrene, polyvinylchloride, polyvinylidene chloride, polyvinyl alcohol, polyvinyl acetate and copolymers and mixtures thereof, as described for example in German published patent application 2 938 896.

If light shades of colour are required, the dyed filler may be mixed in suitable proportions with undyed white pigment.

The coloured coating compositions may be applied to paper, which they itself be white or coloured, by any conventional coating process used in the paper industry. Coated paper dyed according to the present invention has good light fastness and excellent bleeding fastness for example to water, alcohol, milk or soap. Because of the high affinity of these dyestuffs for the filler there are practically no differential migration effects upon drying and level dyeings are obtained even when combinations of dyes are used.

The dyeing is carried out with a high yield and minimal pollution of equipment and waste water. If a cationic dye is added to a coating composition without being fully exhausted on to the filler, of if the composition contains a filler which has been dyed with an insufficiently substantive cationic dyestuff, the dyestuff which is in solution may cause agglomeration and thickening of the composition. The rheological properties of the composition may be so adversely affected that it is no longer possible to apply it by coating and the stability of the composition may be severely reduced. The present invention overcomes this disadvantage, resulting in excellent stability of the coating composition as well as good fastness properties in the dyed paper.

Paper dyed according to the process of the invention may be bleached without difficulty, in contrast to paper coated with compositions containing pigment dyes. This is of considerable importance for the recycling of dyed and coated waste paper.

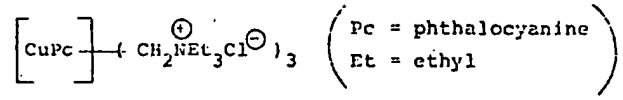
Paper dyed according to the present invention takes print impression very well, and is exceptionally

suitable as copying paper in xerography.

The following Examples in which all parts and percentages are by weight illustrate the invention:

Example 1

285.7 Parts of a 35% aqueous dispersion of kaolin (English China Clay Ltd.), containing 100 parts kaolin dry weight, are stirred at room temperature (20°C) and 10 parts of a 25% aqueous solution of the dye



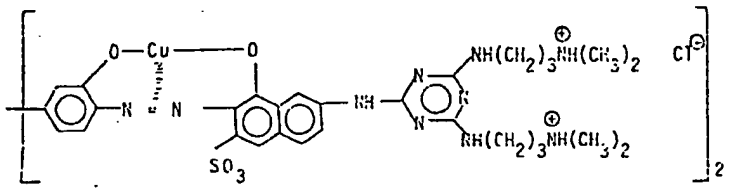
are added. After 2 minutes dyeing time 1.5 parts of a dispersing agent based on sodium polyacrylate (Polysalz F, BASF) are added, followed by 20 parts of a 50% solids synthetic binding agent based on butadiene/styrene (Dow-Latex 620). The pH is adjusted to 8.5 with 25% ammonia. A deep turquoise blue coating composition with a solids content of approx. 40% is obtained.

This composition is applied to uncoated paper of weight 80 g/m^2 by means of a doctor blade, at an application rate of 20 g dry substance per square meter. Finally the paper is dried in a convection drier at 105°C for 60 seconds.

A level and deeply coloured coated paper is obtained, having excellent wet fastness to water and alcohol, as well as good light fasteness.

Example 2

Example 1 is repeated, but using as dyestuff 10 parts of a 20% aqueous solution of:



Example 3

100 Parts chalk (Omyalite 90) is made into a paste with 185 parts water and homogenised with a Roth dispersor until a stable viscosity is obtained (approx. 10 minutes). The dyestuff shown in Example 2 (10 parts) is then added as 20% aqueous solution. After starting for 5 minutes, 1 part dispersing agent (Polysaltz F) is added, and after a further 2 minutes the dyed slurry is filtered.

The filter residue remains dyed deep blue and the filtrate practically colourless even after repeated washing with water. The product may be used as described in Example 1.

CLAIMS

1. A coloured coating composition for paper comprising an aqueous paste or dispersion of a filler which has been dyed with a water-soluble polycationic dyestuff, together with a binding agent.
2. A coating composition according to Claim 1 in which the filler is kaolin, calcium carbonate or talc.
3. A coating composition according to Claim 1 or Claim 2 in which the dyestuff is biscationic.
4. A coating composition according to any one of the preceding claims in which the dyestuff is a metal complex dyestuff.
5. A coating composition according to Claim 4 in which the dyestuff is a 1:1 or 1:2 metal complex azo dye.
6. A coating composition according to any one of the preceding claims in which th dyestuff, as the metal-free cation, has a molecular weight of at least 400.
7. A coating composition according to any one of the preceding claims in which the dyestuff exhausts from an aqueous solution containing 1% dyestuff, based on the weight of filler, on to the filler, at 20-90°C and without the use of dyeing assistants, to an extent of at least 90%.
8. A coating composition according to any one of the preceding claims in which the dyestuff gives an exhaust ratio (ratio of dye exhausted on to substrate to total dye in bath) of 90-100% as defined by DIN 54000 or ISO RIOS/I 1959, part 1, when dyed on to mercerised cotton at 1/1 standard depth from a boiling aqueous electrolyte-free bath at 20:1 liquor to goods ratio, dyeing time 90 minutes.
9. A coating composition according to any one of the preceding claims in which the dyestuff is a phthalocyanine dyestuff containing 2 or more cationic groups which are attached to the periphery of the phthalocyanine ring system.
10. A coating composition according to any one of Claims 1-8 in which the dyestuff has a substantially linear structure comprising three or more homo- or hetero-aromatic rings or fused ring systems joined directly or by bridging groups in such a way that there are two terminal rings or ring systems and one or

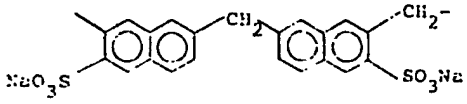
more medial rings or ring systems, there being on average at least 1.3 cationic groups per molecule attached to terminal rings or ring systems, and none elsewhere.

11. A coating composition according to Claim 10 in which the dyestuff has one cationic group on each terminal ring or ring system and none elsewhere.

12. A coating composition according to any one of the preceding claims in which the dyestuff is one of those disclosed in published British Patent Application 2 076 421A, 2 081 734A, 2 082 615A, British Patent 2 019 873 or published European Application 41 040.

13. A coating composition according to any one of the preceding claims, comprising 0.1-10% by weight of a dispersing agent.

14. A coating composition according to Claim 13 in which the dispersing agent is a condensation product of β-naphthalene sulphonic acid with formaldehyde, containing units of structure



15. A coating composition as described in any one of the Examples.

16. A filler selected from kaolin, calcium carbonate, talc, permanent white and titanium dioxide and dyed with a polycationic dyestuff.

17. A dyed filler as described in Example 3.

18. A process for the preparation of coloured, coated paper, comprising the step of applying to paper a coating composition according to any one of Claims 1-15.

19. Coloured paper coated with a coating composition according to any one of Claims 1-15.

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